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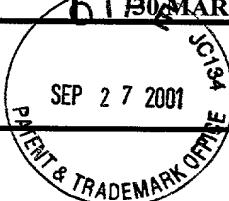
ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

25045-11

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/937817

INTERNATIONAL APPLICATION NO.  
PCT/EPOO/02831INTERNATIONAL FILING DATE  
01 MARCH 2000 (30.03.00)PRIORITY DATE CLAIMED  
31 MARCH 1999 (31.03.99)TITLE OF INVENTION  
OPTICAL WAVE-GUIDEAPPLICANT(S) FOR DO/EO/US  
HORN, Hans-Matthias, et al

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1.  This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2.  This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3.  This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4.  The US has been elected by the expiration of 19 months from the priority date (Article 31).
5.  A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a.  is attached hereto (required only if not communicated by the International Bureau).
  - b.  has been communicated by the International Bureau.
  - c.  is not required, as the application was filed in the United States Receiving Office (RO/US).
6.  An English language translation of the International Application as filed (35 U.S.C. 371(c)(2))
  - a.  is attached hereto.
  - b.  has been previously submitted under 35 U.S.C. 154(d)(4).
7.  Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a.  are attached hereto (required only if not communicated by the International Bureau).
  - b.  have been communicated by the International Bureau.
  - c.  have not been made; however, the time limit for making such amendments has NOT expired.
  - d.  have not been made and will not be made.
8.  An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9.  An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). (unsigned)
10.  An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11.  A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12.  A copy of the International Search Report (PCT/ISA/210).

## \* Items 13 to 20 below concern document(s) or information included:

13.  An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14.  An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15.  A **FIRST** preliminary amendment.
16.  A **SECOND** or **SUBSEQUENT** preliminary amendment.
17.  A substitute specification.
18.  A change of power of attorney and/or address letter.
19.  A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20.  A second copy of the published international application under 35 U.S.C. 154(d)(4).
21.  A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22.  Certificate of Mailing by Express Mail
23.  Other items or information:

I hereby certify that this paper or fee is being  
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service under 37 CFR 1.10 on the date

indicated below and addressed to the  
Commissioner of Patents and Trademarks,

Washington, DC 20231.

*Brigid Mullins*

DATE: 27 September 2001

EXPRESS MAIL NO. ET035783334US

U.S. APPLICATION NO. (IF KNOWN) 37 CFR <b>097957817</b>	INTERNATIONAL APPLICATION NO. <b>PCT/EPOO/02831</b>	ATTORNEY'S DOCKET NUMBER <b>25045-11</b>			
24. The following fees are submitted:		<b>CALCULATIONS PTO USE ONLY</b>			
<b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :</b>					
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... <b>\$1000.00</b> <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... <b>\$860.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... <b>\$710.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... <b>\$690.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... <b>\$100.00</b>					
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>		<b>\$860.00</b>			
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).		<input type="checkbox"/> 20 <input type="checkbox"/> 30 <b>\$0.00</b>			
<b>CLAIMS</b>		<b>NUMBER FILED</b>	<b>NUMBER EXTRA</b>	<b>RATE</b>	
Total claims		17 - 20 =	0	x \$18.00	<b>\$0.00</b>
Independent claims		2 - 3 =	0	x \$80.00	<b>\$0.00</b>
Multiple Dependent Claims (check if applicable)		<input type="checkbox"/>			<b>\$0.00</b>
<b>TOTAL OF ABOVE CALCULATIONS =</b>		<b>\$860.00</b>			
<input type="checkbox"/> Applicant claims small entity status. (See 37 CFR 1.27). The fees indicated above are reduced by 1/2.		<b>\$0.00</b>			
<b>SUBTOTAL =</b>		<b>\$860.00</b>			
Processing fee of <b>\$130.00</b> for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)).		<input type="checkbox"/> 20 <input type="checkbox"/> 30	<b>\$0.00</b>		
<b>TOTAL NATIONAL FEE =</b>		<b>\$860.00</b>			
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).		<input type="checkbox"/>			<b>\$0.00</b>
<b>TOTAL FEES ENCLOSED =</b>		<b>\$860.00</b>			
		<b>Amount to be:</b> <b>refunded</b> <b>\$</b> <b>charged</b> <b>\$</b>			
<p>a. <input checked="" type="checkbox"/> A check in the amount of <b>\$860.00</b> to cover the above fees is enclosed.</p> <p>b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <b>08-0719</b> A duplicate copy of this sheet is enclosed.</p> <p>d. <input type="checkbox"/> Fees are to be charged to a credit card. <b>WARNING: Information on this form may become public. Credit card information should not be included on this form.</b> Provide credit card information and authorization on PTO-2038.</p>					
<p><b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</b></p>					
<p>SEND ALL CORRESPONDENCE TO:</p> <p><b>John B. Hardaway, III</b>  <b>NEXSEN PRUET JACOBS &amp; POLLARD, LLC</b>  <b>PO Box 10107</b>  <b>Greenville, SC 29603</b></p>					
 <b>SIGNATURE</b>					
<p><b>J. Herbert O'Toole</b></p> <p>NAME</p> <p><b>31,404</b></p> <p>REGISTRATION NUMBER</p> <p><b>27 Sept 2001</b></p> <p>DATE</p>					



09/937817

JC05 Rec'd PCT/PTO 27 SEP 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: HORN, Hans-Matthias, et al. ) Attorney Docket: 25045-11  
International Serial No.: PCT/EP00/02831 )  
International Filing Date: 30 March 2000 ) Examiner: Unknown  
Title: Optical Wave-Guide ) Art Unit: Unknown  
 )

Honorable Commissioner for Patents  
Washington, DC 20231

**PRELIMINARY AMENDMENT**

Dear Sir:

Prior to the examination of the subject application, please enter the following amendments.

In the Specification

Please enter the substitute specification attached hereto.

In the Claims

Please cancel original claims 1-12. Please enter new claims 13-29.

In the Abstract

Please enter the substitute abstract attached hereto.

**REMARKS**

This application is filed in the United States Patent and Trademark office under 35 USC 371 arising from PCT/EP00/02831, claiming priority of German Patent Application DE 199 14 743.4. Attached hereto is a translation into English of the German language PCT Specification and claims and a substitute specification formatted in accordance with U.S. practice. Also enclosed are new claims eliminating, *inter alia*; multiple dependent claims.

Respectfully submitted,

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September 27, 2001



## OPTICAL WAVE-GUIDE

### BACKGROUND OF THE INVENTION

### FIELD OF THE INVENTION

**[0001]** The present invention relates to optical wave-guides having a plastic optical fiber comprising a fiber core and a fiber cladding having a single- or multilayer structure, and at least one protective sheathing. The fiber cladding or at least its outer layer may be made of a fluorine-containing plastic. For the protective sheathing of the fiber core, polyamide may be used.

### BACKGROUND AND PRIOR ART

**[0002]** Plastic optical fibers are used in the field of telecommunication as an optical transmission element which is not susceptible to interference and is easy to handle wherever the distance between the transmitting unit and the receiving unit is only a few meters up to a maximum of 100 - 150 meters. In the fields of traffic engineering / automobile manufacturing (data and signal transmission in vehicles, aeroplanes, ships, etc.), lighting (variable message signs), automatic control engineering (machine control) and sensor technology too, plastic optical fibers are gaining increasing importance [Draht (Wire) 46 (1995) 4, pp. 187-190].

**[0003]** A plastic optical fiber used for data and signal transmission consists of a fiber core (outer diameter  $\varnothing_{\text{core}} \approx 980 \mu\text{m}$ ), which is often made of polymethyl methacrylate (PMMA; refractive index  $n_{\text{PMMA}} = 1.49$ ), and a fiber cladding (outer diameter  $\varnothing_{\text{cladding}} \approx 1000 \mu\text{m}$ ) having a single- or multilayer structure which concentrically encloses the fiber core. Fluorine-containing plastics whose refractive index  $n_{\text{cladding}}$  ranges from 1.35 to 1.42 are mainly used as the cladding material. The optical absorption of such a plastic wave-guide is typically 130 - 150 db/km ( $\lambda = 650 \text{ nm}$ ), the minimum bending radius is approx. 5 - 10 mm.

**[0004]** To protect the sensitive plastic optical fiber from mechanical, thermal and chemical effects, it is provided with a plastic cladding hereafter referred to as protective sheathing which may have a multilayer structure (c.f. WO 99/12063). The protective sheathing (outer diameter  $\varnothing_{\text{wave-guide}} \approx 1.5 - 2.2 \text{ mm}$ ) coated by means of an extruder may, depending on the intended use or application, be made of polyethylene (PE), polyvinyl chloride (PVC), ethylene vinylacetate (EVA) or polyamide (PA), for example.

**[0005]** In the field of automobile manufacturing, polyamides are used as a protective sheathing material, as it meets the requirements there in terms of mechanical strength (tensile strength, lateral compression strength), maximum application temperature, and chemical resistance. However, the

poor adhesion of the polyamide protective sheathing to the plastic optical fiber whose fiber cladding is made of a fluorine-containing polymer causes problems. The weak adhesion of the protective sheathing has a particularly adverse effect when the optical wave-guide (plastic optical fiber plus protective sheathing) is installed in an environment (e. g. passenger compartment of a motor vehicle) which is subject to large variations in temperature and the plastic optical fiber moves in relation to the protective sheathing due to the fiber's varying thermal expansion behavior and the poor adhesion of the polyamide to the fluoropolymer. As a result, the distance between the face of the plastic optical fiber and the transmitting and receiving elements (LED / p-i-n diode) may increase to such an extent that unacceptably high losses in intensity occur which may lead to the failure of the data transmission line. Moreover, there is a risk that the transmitting or receiving elements might be damaged if the plastic optical fiber moves too far out of the protective sheathing.

[0006] To suppress this effect which is referred to as pistonning of the plastic optical fiber, connectors, couplers or holders are used which apply large clamping or crimping forces to the protective sheathing to thereby increase the friction between the protective sheathing and the plastic optical fiber. The resulting deformation of the interface between fiber core and fiber cladding leads, however, to an increased signal attenuation.

[0007] Removing the protective layer within the connector avoids pistonning but involves the risk that the fiber cladding might be damaged during the assembly due to improper handling of the shouldering tool equipped with a pair of knife edges.

[0008] The clamping or crimping forces applied by the connector to the optical wave-guide can also be reduced by positively anchoring the plastic optical fiber in a tapered hole in the connector housing. It was proposed, for example, that the face of the plastic optical fiber should be partly melted by means of a hot plate, the resulting melting build-up should be pressed into the connector hole tapering inwardly to thereby firmly anchor the plastic optical fiber to the connector housing. In the partly molten and thus deformed area, the geometry of the plastic optical fiber may possibly substantially deviate from the cylindrical geometry which enables total reflection so that increased losses of intensity occur in the connector housing.

[0009] EP 0 649 738 A1 discloses that a condensation product of polyamide and polyvinylidene chloride may be prepared by admixing a polyglutarimide to the polyamide. By a single-step extrusion process, for example, a two-layer composite can be made from a polyamide and a polyvinylidene fluoride and a three-layer composite can be made from a polyamide, an adhesion promoter layer of a polyamide-polyglutarimide blend and a polyvinylidene fluoride. Polyglutarimides are also known as polymethacryl imides (PMMI).

[00010] In the extrusion processing of plastic optical fibers it is important that the protective sheathing which directly contacts the fiber cladding is applied at a temperature as low as possible. The glass-transition temperatures of the fluorine-containing polymers of the fiber cladding are in close proximity to those of the fiber core material (PMMA: 106 °C), i. e. between 80 and 120 °C. The thickness of the fiber cladding is, however, only 10 µm, its optical properties are precisely adjusted and can easily be influenced or changed by thermal or chemical effects. Therefore, the materials of the protective sheathing must be extruded at a melting temperature as low as possible.

[00011] When the inventors of the present application tested blends of PMMI (Pleximid 130, manufactured by Röhm, Germany) and low-viscous polyamide 12 (relative viscosity 1.65, 0.5 % measured in *m*-cresol), they could find that the high blend viscosity resulted in quite high melting temperatures in the cable extrusion of plastic optical fibers and an irreversible increase in the optical absorption of the fiber. Blends of polyamide 12 and PMMI therefore can not be used as materials for the protective sheathing.

[00012] It is noted that the polyglutarimides given as examples of EP 0 649 738 A1 in the Table on page 6 have a very high viscosity and cannot be used as an intermediate layer for a three-layer process or as a component in the blend with polyamide 12 for the plastic optical fiber extrusion.

[00013] EP 0 767 190 A1 discloses the use of polyamide adhesion promoters for the manufacture of multilayer polymer pipes or piping, i. e. gasoline or coolant lines for automotive manufacturing. The polyamides used here have usually high viscosity. Moreover, no optical properties of the layers are required. But the polyamides described in EP 0 767 190 A1 have an excess of terminal amino groups. In extrusion tests with plastic optical fibers using the adhesion promoter disclosed in EP 0 767 190 A1 which were performed by the inventors of the present application, acceptable extrusion temperatures were achieved so that the optical fiber was not thermically damaged, but when the optical fiber was subsequently stored at a high temperature (80 °C, 24 hours), the outer layer of the fiber, i. e. the cladding, turned brown. This seemed to have been caused by a diffusion of the monomers into the cladding and a subsequent chemical reaction. The discoloration had an adverse effect on the optical properties of the fiber. The polyamide moulding materials according to EP 0 767 190 A1 have thus to be ruled out as an adhesion promoter or protective layer for plastic optical fibers.

## BRIEF SUMMARY OF THE INVENTION

[00014] It is therefore the object of the present invention to provide an optical wave-guide with

a slight relative motion even at large variations in temperature. The moulding material making up the protective sheathing should adhere well to the fiber cladding and should not chemically attack it. In addition, it should be ensured that the transmission behavior and the attenuation properties of the optical wave-guide largely correspond to those of the plastic optical fiber which is not enclosed by the moulding material.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

**[00015]** Fig. 1 is a cross-section of an optical wave guide fiber.

#### **DETAILED DESCRIPTION OF THE INVENTION**

**[00016]** The present invention relates therefore to an optical wave-guide 1 comprising a plastic optical fiber 2, 3 including a fiber core 2 and a fiber cladding 3 having a single- or multilayer structure, and at least one protective sheathing 4 enclosing the plastic optical fiber 2, 3. The fiber cladding 3 or at least its outer sheathing of a fluorine-containing plastic and the protective sheathing 4 are mainly made of polyamides (PA), preferably PA 11, PA 12, PA 610, PA 612, PA 1212 or the copolyamides PA 6/12, PA 6/9/6, PA 6/9/12, PA 610/6, PA 610/11, PA 610/12, PA 612/6, PA 612/11, PA 612/12 or mixtures thereof as well as other homopolyamides or copolyamides having a melting point of less than 220 °C, preferably less than 210 °C, particularly preferably less than 200 °C, and the protective sheathing 4 is self-adhesively applied to the fiber cladding 3. The maximum concentration of the carboxyl terminal groups of the polyamide used is 15  $\mu\text{eq/g}$  and the concentration of the amino terminal groups is in the range of 50  $\mu\text{eq/g}$  to 300  $\mu\text{eq/g}$ .

**[00017]** The polyamides used according to the invention have a low viscosity so that they can be extruded at a melting temperature as low as possible. Specifically, the polyamides according to the invention have a viscosity below 2.0, in particular below 1.8 and particularly preferably a viscosity of 1.4 to 1.8 (relative viscosity: 0.5 % measured in *m*-cresol). This serves to improve the quality of processing. A temperature test (80 °C, 24 hours; see below) showed no discoloration of the outer layer of the fiber, i. e. the cladding, and hence no adverse effect on the optical properties of the fiber.

**[00018]** Due to the good adherence of the protective sheathing made of a modified PA to the fiber cladding of the plastic optical fiber, a connector slipped on the end side needs to apply clearly lower clamping or crimping forces to the optical wave-guide to avoid the effect referred to as pistonning. This reduces the signal attenuation in the plastic optical fiber which is caused by outer forces and allows the use of connectors or holders which have a comparatively simple structure and are therefore cheaper. Moreover, the protective sheathing near the connector no longer needs to be removed. Even after 24-hour storage of the optical wave-guide at a temperature of 80 °C there is no

increase in signal attenuation induced by chemical action. Specifically, there is specifically no discoloration of the fiber cladding.

**[00019]** The invention will now be explained with reference to the drawing and the embodiments, the single Figure showing the cross section of an embodiment of the optical wave-guide (A plastic optical fiber simplex wave-guide).

**[00020]** The optical wave-guide 1 which is shown schematically and not true to scale in a cross-sectional view in Fig. 1 is used typically as a transmission element to transmit data and signals free from unwanted signals within the passenger compartment of a motor vehicle. As a light-guiding structure, the wave-guide 1 contains a so-called step index profile plastic optical fiber which consists in the embodiment shown of a PMMA fiber core 2 ( $\varnothing_{\text{core}} = 980 \mu\text{m}$ , refractive index  $n_{\text{core}} = 1.49$ ) and a fiber cladding 3 ( $\varnothing_{\text{cladding}} = 1000 \mu\text{m}$ , refractive index  $n_{\text{cladding}} = 1.35 - 1.42$ ) made of a fluorine-containing polymer which has a single- or multilayer structure. As the plastic PMMA is very easy to cut and grind, the processing of the fiber face (which must be clean, smooth and free from striations) takes little time. In addition, despite its relatively large diameter of approx. 1 mm., the plastic optical fiber 2, 3 has an extremely high bending strength which facilitates assembly and installation. The optical absorption of the fiber core 2 is typically 70 - 100 db/km ( $\lambda = 570 \text{ nm}$ ) or 125 - 150 db/km ( $\lambda = 650 \text{ nm}$ ).

**[00021]** The fluorine-containing polymers used as the cladding material or as the material for the outer cladding layer may be pure polymers, copolymers of fluorine-containing monomers as well as copolymers of fluorine-containing monomers with acrylic acid and acrylates as well as mixtures of such polymers or copolymers. Vinylidene fluoride, tetrafluoroethylene, hexafluoropropene, methacrylic acid-tetrafluoropropylester, methacrylic acid-pentafluoropropylester, methacrylic acid-trifluoroethylester, methacrylic acid-heptadecafluorodecylester as well as mixtures or copolymerisates thereof, alternatively also acrylic acid- or acrylate-modified polymers, copolymers or polymer mixtures may be used in particular.

**[00022]** The outer diameters of the fiber core 2 and the fiber cladding 3 meet the standard specified in IEC 60 793-2 (outer diameter of cladding  $\varnothing_{\text{cladding}} = 1000 \pm 60 \mu\text{m}$ , the core diameter  $\varnothing_{\text{core}}$  should typically be smaller than  $\varnothing_{\text{cladding}}$  by 10 - 20  $\mu\text{m}$ ; numerical aperture  $0.5 \pm 0.15$ ). It is of course also possible to select the dimensions of the fiber core 2 and the fiber cladding 3 according to the other standard values ( $\varnothing_{\text{cladding}} = 750 \pm 45 \mu\text{m}$  or  $500 \pm 30 \mu\text{m}$ ) or to adapt the dimensions to the commercial step index profile plastic optical fibers ( $\varnothing_{\text{cladding}} = 75 \mu\text{m} / 125 \mu\text{m} / 250 \mu\text{m} / 380 \mu\text{m} /$

1500 µm / 2000 µm / 3000 µm).

**[00023]** The moulding material enclosing the plastic optical fiber which is applied by co- or tandem extrusion protects the sensitive plastic optical fiber 2, 3 from outer influences. Its thickness is selected according to the above standard such that the outer diameter of the wave-guide  $\varnothing_{\text{wave-guide}}$  is  $2.2 \pm 0.1$  mm ( $\varnothing_{\text{cladding}} = 1000$  µm or  $\varnothing_{\text{cladding}} = 750$  µm) or  $\varnothing_{\text{wave-guide}} = 1.5 \pm 0.1$  mm ( $\varnothing_{\text{cladding}} = 500$  µm).

**[00024]** The moulding material 4 which is used as the protective sheathing and particularly well adheres to the fluorine-containing polymer of the fiber cladding 3 is made of a modified PA whose maximum concentration of carboxyl terminal groups is 15 µeq/g and whose concentration of amino terminal groups is in the range of 50 - 300 µeq/g. The above concentration of amino terminal groups is adjusted by an aminic chain transfer agent added to the not yet completely polymerized PA (single polymerization of the chain transfer agent). Examples of chain transfer agents are hexyl amine, octyl amine, ethyl hexyl amine, tridecyl amine, dibutyl amine, stearyl amine and other aliphatic, cycloaliphatic or aromatic monoamines having 2 - 44 C atoms, in particular 4 - 36 C atoms, as well as diamines such as 1,4-diaminobutane, 1,6-diaminohexane, diaminocyclohexane, 1,10-diaminodecane, 1,12-diaminododecane, *m*- or *p*-xylylene diamine, cyclohexyl dimethylene diamine, bis-(*p*-aminocyclohexyl) methane as well as other aliphatic, cycloaliphatic or aromatic amines having 2 - 44 C atoms, in particular 6 - 36 C atoms, and the excess of an aminic difunctional monomer which is the main component of the polyamide.

**[00025]** Suitable polyamides for the purposes of the invention are homo- and copolyamides which can be processed at sufficiently low temperatures, i. e. at a maximum of 220 °C, so as not to damage the cladding and fiber core of the plastic optical fiber. According to the invention it is essential that the polyamides used have a relative viscosity below 2.0, in particular below 1.8 and particularly preferably 1.4 - 1.8 (relative viscosity: 0.5 % measured in *m*-cresol at 20 °C).

**[00026]** Such polyamides may also be made up of polyamide-forming monomers such as caprolactam, laurine lactam, amino hexanoic acid, amino undecanoic acid, dodecanedioic acid, dimeric acid, terephthalic acid, isophthalic acid, cyclohexane dicarboxylic acid, naphthalene dicarboxylic acid, tert-butyl isophthalic acid, phenylindane dicarboxylic acid, diaminobutane, hexamethylene diamine, methyl pentamethylene diamine, 3,3-dimethyl-4,4-xylylene diamine, 2,2-bis(*p*-aminocyclohexyl) propane, bis(*p*-aminocyclohexyl) methane, isophorone diamine, polypropyleneglycol diamine, norbonane diamine, 1,3-bis(aminomethyl) cyclohexane, TCD diamine if they have a melting point up to a maximum of 220 °C, preferably below 210 °C and particularly

preferably below 200 °C. These include according to the invention in particular PA 11, PA 12, PA 610, PA 612, PA 1212 or the copolyamides PA 6/12, PA 6/9/6, PA 6/9/12, PA 610/6, PA 610/11, PA 610/12, PA 612/6, PA 612/11, PA 612/12 or mixtures thereof, PA 12 being particularly preferred.

**[00027]** To the polyamides having the above structure, normal additives such as UV and heat stabilizers, crystallization promoters, softeners, flameproofing agents, external lubricants, and inorganic fillers may be added.

**[00028]** The following method was used to test the adherence of the protective sheathing 4 made of a modified polyamide to the fiber cladding 3:

- partial shouldering of the protective sheathing of a wave-guide approx. 500 mm in length in such a way that the length of the remaining protective sheathing is approx. 30 mm;
- leading the shouldered portion of the wave-guide through the hole of a plate, the diameter of the hole being  $\approx$ 1.1 mm which is somewhat larger than the outer diameter of the fiber cladding;
- chucking the shouldered end of the wave-guide into a tensile testing machine (drawing-off rate: 10 mm/min); and
- measuring the tensile force at which the protective sheathing becomes detached from the cladding of the plastic optical fiber.

The PA 12 types given in the Table below were subjected to the test.

Polymer	Concentration of NH <sub>2</sub> terminal groups	Concentration of COOH terminal groups	Relative viscosity: 0.5 % in <i>m</i> -cresol at 20 °C	
PA No. 1	10	95	1.65	PA not according to the invention
PA No. 2	95	<15	1.66	PA according to the invention
PA No. 3	134	<5	1.58	PA according to the invention
PA No. 4	173	<5	1.47	PA according to the invention

[00029] The test showed that the tensile force required for stripping the protective sheathing made of PA No. 1 amounted to a minimum of 11 N (no adherence), typically 40 - 50 N and a maximum of 51 N, due to the very different adherence of the protective sheathing to the respective plastic optical fiber from specimen to specimen. The stripping forces measured for wave-guides with the protective PA sheathings according to the invention ranged from 68 - 75 N and hence varied to a clearly less extent. The measured maximum value of the stripping force of 75 N is surprising all the more so as the extrusion temperature for the moulding material making up the protective sheathing was to amount to only approx. 185 - 200 °C due to the comparatively low glass-transition temperature of the PMMA ( $T_G \approx 100 - 110$  °C) used as the core material.

[00030] A comparatively large stripping force was also measured for an optical wave-guide whose protective sheathing was made of the PA disclosed in EP 0 767 190 A1. However, this PA is not suitable for the above applications, as the heat storage (24 hours at 80 °C) of wave-

guides having an equivalent structure resulted in a browning of the outer cladding area.

**[00031]** The following three typical examples of wave-guides ( $\mathcal{O}_{\text{cladding}} = 1000 \mu\text{m}$ ,  $\mathcal{O}_{\text{protective sheathing}} = 2.2 \text{ mm}$ ) were tested:

Optical wave-guide: type SB-1000, Asahi Chemical Industry Co., Ltd.; moulding material: Grilamid L16A (PA according to the invention), EMS-Chemie AG, CH -7013 Domat/Ems.

Processing temperature of the moulding material:  $T = 190 \text{ }^{\circ}\text{C}$ , processing speed: 60 m/min, stripping force: 68 - 75 N (average: 73 N).

Optical wave-guide: SB-1000; moulding material: Grilamid L16LM (PA not according to the invention), EMS-Chemie AG.

Processing temperature:  $T = 190 \text{ }^{\circ}\text{C}$ , processing speed: 60 m/min, stripping force: 48 - 51 N (average: 49 N).

Optical wave-guide: type TB-1000, Asahi Chemical Industry Co., Ltd.; moulding material: Grilamid L16LM (PA not according to the invention).

Processing temperature:  $T = 190 \text{ }^{\circ}\text{C}$ , processing speed: 60 m/min, stripping force: 7 - 18 N (average: 11 N).

**[00032]** It is to be understood that the invention is not limited to the embodiments described above. Without deviating from the scope of the invention, it is therefore possible

- to give the protective sheathing 4 of the optical wave-guide 1 a multilayer structure (see particularly WO 99/1203) or to provide it with a PVC cladding of  $\approx 1 - 2 \text{ mm}$  in thickness;
- to embed reinforcing elements, in particular glass fibers, carbon fibers or mineral fibers, in the protective sheathing 4;
- to admix fillers (carbon black, talcum, etc.) in the protective sheathing material; and
- to use one or several of the optical wave-guides 1 as light transmitting elements in the simplex, duplex, twin or hybrid cables known as described in A. Weinert:

Kunststofflichtwellenleiter - Grundlagen, Komponenten, Installation (Plastic optical fibers: Fundamentals, Components, Installation), MCD Verlag, Pub. 1998, pp. 55 - 62.

## CLAIMS

13. An optical wave guide having at least one plastic optical fiber comprising a plastic optical fiber core, a fluorine-containing fiber cladding and a protective sheath self-adhesively applied to said at least one plastic optical fiber, wherein said protective sheath comprising polymeric compounds selected from the group consisting of polyamides, copolyamides and mixtures thereof having a melting point less than 220°C a concentration of amino terminal groups between 50 and 300  $\mu\text{eq/g}$  and a maximum concentration of carboxyl terminal groups no greater than 15  $\mu\text{eq/g}$ .

14. An optical wave guide according to claim 13 wherein said polymeric compounds have a melting point less than 210°C.

15. An optical wave-guide according to claim 13 wherein said polyamides are selected from the group consisting of PA 11, PA 12, PA 610, PA 612 and PA 1212.

16. An optical wave-guide according to claim 13 wherein said copolyamides are selected from the group consisting of PA 6/12, PA 6/9/6, PA 6/9/12, PA 610/6, PA 610/11, PA 610/12, PA 612/6, PA 612/11, PA 612/12 and mixtures thereof.

17. An optical wave guide according to claim 13 wherein at least one polyamide, copolyamide or mixture comprises PA 12.

18. An optical wave-guide according to claim 15 wherein the concentration of amino terminal groups is between 90 and 250  $\mu\text{eq/g}$ .

19. An optical wave-guide according to claim 13 wherein said protective sheath further comprises at least one additive selected from the group consisting of UV stabilizers, heat stabilizers, crystallization promoters, softeners, flame retardants, external lubricants and inorganic fillers.

20. An optical wave-guide according to claim 13 wherein said plastic fiber core is formed from polymethylmethacrylate.

21. An optical wave-guide according to claim 13 wherein said plastic optical fiber has an outer diameter of between approximately 75 and approximately 3000  $\mu\text{m}$ .

22. An optical wave-guide according to claim 13 wherein the thickness of the fluorine-container fiber cladding is between 5 and 10  $\mu\text{m}$ .

23. A protective sheath for an optical wave guide having at least one plastic optical fiber comprising a plastic optical fiber core and a fluorine-containing fiber cladding, said sheath comprising polymeric compounds selected from the group consisting of polyamides,

copolyamides and mixtures thereof having a melting point less than 220°C a concentration of amino terminal groups between 50 and 300  $\mu\text{eq/g}$  and a maximum concentration of carboxyl terminal groups no greater than 15  $\mu\text{eq/g}$ .

24. A protective sheath according to claim 23 wherein said polymeric compounds have a melting point less than 210°C.

25. A protective sheath according to claim 23 wherein said polyamides are selected from the group consisting of PA 11, PA 12, PA 610, PA 612 and PA 1212.

26. A protective sheath according to claim 23 wherein said copolyamides are selected from the group consisting of PA 6/12, PA 6/9/6, PA 6/9/12, PA 610/6, PA 610/11, PA 610/12, PA 612/6, PA 612/11, PA 612/12 and mixtures thereof.

27. A protective sheath according to claim 23 wherein at least one polyamide, copolyamide or mixture comprises PA 12.

28. A protective sheath according to claim 23 wherein the concentration of amino terminal groups is between 90 and 250  $\mu\text{eq/g}$ .

29. A protective sheath according to claim 23 wherein said protective sheath further comprises at least one additive selected from the group consisting of UV stabilizers, heat stabilizers, crystallization promoters, softeners, flame retardants, external lubricants and inorganic fillers.

## ABSTRACT

An optical wave-guide having a plastic core and cladding which has an improved sheathing with improved adhesion to the cladding. The sheathing is a polyamide, copolyamide or mixtures thereof having no more than 15  $\mu\text{eq/g}$  of carboxyl terminal groups, 50 to 300  $\mu\text{eq/g}$  of amino terminal groups and a melting point less than 220°C. The sheathing adheres and shows higher resistance to pistonning when the wave-guide is heat cycled.

YPT.

09/937817  
JC05 Rec'd PCT/PTO 27 SEP 2001

Applicant: EMS-CHEMIE AG  
Our Ref.: 91250/US (BE/ST)

28.08.2001

Patent specification

5 The present invention relates to optical wave-guides having a plastic optical fiber comprising a fiber core and a fiber cladding having a single- or multilayer structure, and at least one protective sheathing. The fiber cladding or at least its outer layer may be made of a fluorine-containing plastic. For the protective sheathing of the fiber core, polyamide may be used.

10 Plastic optical fibers are used in the field of telecommunication as an optical transmission element which is insusceptible to interference and is easy to handle wherever the distance between the transmitting unit and the receiving unit is only a few meters up to a maximum of 100 - 150 meters. In the fields of traffic engineering / car manufacturing (data and signal transmission in vehicles, aeroplanes, ships, etc.), lighting (variable message signs), automatic control engineering (machine control) and sensor technology too, plastic optical fibers are gaining increasing importance [Draht (Wire) 46 (1995) 4, pp. 187-190].

15 A plastic optical fiber used for data and signal transmission consists of a fiber core ( $\mathcal{O}_{\text{core}} \approx 980 \mu\text{m}$ ), which is often made of polymethyl methacrylate (PMMA; refractive index  $n_{\text{PMMA}} = 1.49$ ), and a fiber cladding (outer diameter  $\mathcal{O}_{\text{cladding}} \approx 1000 \mu\text{m}$ ) having a single- or multilayer structure which concentrically encloses the fiber core. Fluorine-containing plastics whose refractive index  $n_{\text{cladding}}$  ranges from 1.35 to 1.42 are mainly used as the cladding material. The optical absorption of such a plastic wave-guide is typically 130 - 150 db/km ( $\lambda = 650 \text{ nm}$ ), the minimum bending radius is approx. 5 - 10 mm.

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25 To protect the sensitive plastic optical fiber from mechanical, thermal and chemical effects, it is provided with a plastic cladding hereafter referred to as protective sheathing which may have a multilayer structure (WO 99/12063). The protective sheathing (outer diameter  $\mathcal{O}_{\text{wave-guide}} \approx 1.5 - 2.2 \text{ mm}$ ) coated by means of an extruder may, depending on the intended use or application, be 30 made of polyethylene (PE), polyvinyl chloride (PVC), ethylene vinylacetate (EVA) or polyamide

(PA), for example.

In the field of car manufacturing, polyamides are used as a protective sheathing material, as it meets the requirements there in terms of mechanical strength (tensile strength, lateral compression strength), maximum application temperature, and chemical resistance. However, the poor adhesion of the polyamide protective sheathing to the plastic optical fiber whose fiber cladding is made of a fluorine-containing polymer causes problems. The weak adhesion of the protective sheathing has a particularly adverse effect when the optical wave-guide (plastic optical fiber plus protective sheathing) is installed in an environment (e. g. passenger compartment of a motor vehicle) which is subject to large variations in temperature and the plastic optical fiber moves in relation to the protective sheathing due to the fiber's varying thermal expansion behavior and the poor adhesion of the polyamide to the fluoropolymer. As a result, the distance between the face of the plastic optical fiber and the transmitting and receiving elements (LED / p-i-n diode) possibly increases to such an extent that unacceptably high intensity losses occur which may lead to the failure of the data transmission line. Moreover, there is a risk that the transmitting or receiving elements might be damaged if the plastic optical fiber moves too far out of the protective sheathing.

To suppress this effect which is referred to as "pistoning" of the plastic optical fiber, connectors, 20 couplers or holders are used which apply large clamping or crimping forces to the protective sheathing to thereby increase the friction between the protective sheathing and the plastic optical fiber. The resulting deformation of the interface between fiber core and fiber cladding leads, however, to an increased signal attenuation.

25 Removing the protective layer within the connector avoids pistoning but involves the risk that the fiber cladding might be damaged during the assembly due to improper handling of the shoulder tool equipped with a pair of knives.

30 The clamping or crimping forces applied by the connector to the optical wave-guide can also be reduced by positively anchoring the plastic optical fiber in a tapered hole of the connector housing. It was proposed, for example, that the face of the plastic optical fiber should be partly melted by means of a hot plate, the resulting melting build-up should be pressed into the

connector hole tapering inwards to thereby firmly anchor the plastic optical fiber to the connector housing. In the partly molten and thus deformed area, the geometry of the plastic optical fiber may possibly substantially deviate from the cylinder geometry enabling total reflection so that increased intensity losses occur in the connector housing.

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EP 0 649 738 A1 discloses that a non-positive compound of polyamide and polyvinylidene chloride may be prepared by admixing a polyglutarimide to the polyamide. By a single-step extrusion process, for example, a two-layer composite can be made from a polyamide and a polyvinylidene fluoride and a three-layer composite can be made from a polyamide, an adhesion promoter layer of a polyamide-polyglutarimide blend and a polyvinylidene fluoride. Polyglutarimides are also known as polymethacryl imides (PMMI).

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In the extrusion processing of plastic optical fibers it is important that the protective sheathing which directly contacts the fiber cladding is applied at a temperature as low as possible. The glass-transition temperatures of the fluorine-containing polymers of the fiber cladding are in close proximity to those of the fiber core material (PMMA: 106 °C), i. e. between 80 and 120 °C. The thickness of the fiber cladding is, however, only 10 µm, its optical properties are precisely adjusted and can easily be influenced or changed by thermal or chemical effects. Therefore, the materials of the protective sheathing must be extruded at a melting temperature as low as possible.

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When the inventors of the present application tested blends of PMMI (Pleximid 130, manufactured by Röhm, Germany) and low-viscous polyamide 12 (relative viscosity 1.65, 0.5 % measured in m-cresol), they could find that the high blend viscosity resulted in clearly high melting temperatures in the cable extrusion of plastic optical fibers and an irreversible increase in the optical absorption of the fiber. Blends of polyamide 12 and PMMI can therefore not be used as materials for the protective sheathing.

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Incidentally, the polyglutarimides given as examples of EP 0 649 738 A1 in the Table on page 6 have a very high viscosity and cannot be used as an intermediate layer for a three-layer process or as a component in the blend with polyamide 12 for the plastic optical fiber extrusion.

EP 0 767 190 A1 discloses the use of polyamide adhesion promoters for the manufacture of multilayer polymer pipes or piping, i. e. gasoline or coolant lines for the car manufacture. The polyamides used here have usually no low viscosity. Moreover, no optical properties of the layers are required either. But the polyamides described in EP 0 767 190 A1 have an excess of amino 5 terminal groups. In extrusion tests with plastic optical fibers using the adhesion promoter disclosed in EP 0 767 190 A1 which were performed by the inventors of the present application, acceptable extrusion temperatures were achieved so that the optical fiber was not thermically damaged, but when the optical fiber was subsequently stored at a high temperature (80 °C, 24 hours), the outer layer of the fiber, i. e. the cladding, turned brown. This seemed to have been 10 caused by a diffusion of the monomers into the cladding and a subsequent chemical reaction. The discolouration had an adverse effect on the optical properties of the fiber. The polyamide moulding materials according to EP 0 767 190 A1 have thus to be ruled out as an adhesion promoter or protective layer for plastic optical fibers.

15 It is therefore the object of the present invention to provide an optical wave-guide with a slight relative motion even at large variations in temperature. The moulding material making up the protective sheathing should well adhere to the fiber cladding and should not chemically attack it. In addition, it should be ensured that the transmission behavior and the attenuation properties of 20 the optical wave-guide largely correspond to those of the plastic optical fiber which is not enclosed by the moulding material.

The present invention relates therefore to an optical wave-guide 1 comprising a plastic optical fiber 2, 3 including a fiber core 2 and a fiber cladding 3 having a single- or multilayer structure, and at least one protective sheathing 4 enclosing the plastic optical fiber 2, 3. The fiber cladding 25 3 or at least its outer sheathing of a fluorine-containing plastic and the protective sheathing 4 are mainly made of polyamides (PA), preferably PA 11, PA 12, PA 610, PA 612, PA 1212 or the copolyamides PA 6/12, PA 6/9/6, PA 6/9/12, PA 610/6, PA 610/11, PA 610/12, PA 612/6, PA 612/11, PA 612/12 or mixtures thereof as well as other homopolyamides or copolyamides having 30 a melting point of less than 220 °C, preferably less than 210 °C, particularly preferably less than 200 °C, and the protective sheathing 4 is self-adhesively applied to the fiber cladding 3. The maximum concentration of the carboxyl terminal groups of the polyamide used is 15 µeq/g and the concentration of the amino terminal groups is in the range of 50 µeq/g to 300 µeq/g.

The optical wave-guide as claimed in Claim 1 meets the above requirements.

The polyamides used according to the invention have a low viscosity so that they can be extruded at a melting temperature as low as possible. Specifically, the polyamides according to the invention have a viscosity below 2.0, in particular below 1.8 and particularly preferably a viscosity of 1.4 to 1.8 (relative viscosity: 0.5 % measured in m-cresol). This serves to improve the quality of processing. A temperature test (80 °C, 24 hours; see below) showed no discoloration of the outer layer of the fiber, i. e. the cladding, and hence no adverse effect on the optical properties of the fiber.

The subclaims include advantageous embodiments of the invention.

Due to the good adherence of the protective sheathing made of a modified PA to the fiber cladding of the plastic optical fiber, a connector slipped on the end side needs to apply clearly lower clamping or crimping forces to the optical wave-guide to avoid the effect referred to as pistonning. This reduces the signal attenuation in the plastic optical fiber which is caused by outer forces and allows the use of connectors or holders which have a comparatively simple structure and are therefore cheaper. Moreover, the protective sheathing near the connector is no longer needed to be removed. Even a 24-hour storage of the optical wave-guide at a temperature of 80 °C results in no increase in signal attenuation induced by chemical processes. There is specifically no discoloration of the fiber cladding.

The invention will now be explained with reference to the drawing and the embodiments, the single Figure showing the cross section of an embodiment of the optical wave-guide (“plastic optical fiber simplex wave-guide”).

The optical wave-guide 1 which is shown schematically and not true to scale in a cross-sectional view in Fig. 1 is particularly used as a transmission element to transmit data and signals freely from unwanted signals within the passenger compartment of a motor vehicle. As a light-guiding structure, the wave-guide 1 contains a so-called step index profile plastic optical fiber which consists in the embodiment shown of a PMMA fiber core 2 ( $\mathcal{O}_{\text{core}} = 980 \mu\text{m}$ , refractive index

5  $n_{\text{core}} = 1.49$ ) and a fiber cladding 3 ( $\mathcal{O}_{\text{cladding}} = 1000 \mu\text{m}$ , refractive index  $n_{\text{cladding}} = 1.35 - 1.42$ ) made of a fluorine-containing polymer which has a single- or multilayer structure. As the plastic PMMA is very easy to cut and grind, the processing of the fiber face (which must be clean, smooth and free from striae) takes only little time. In addition, despite its relatively large diameter of approx. 1 mm the plastic optical fiber 2, 3 has an extremely high bending strength facilitating the assembly and installation. The optical absorption of the fiber core 2 is typically 70 - 100 dB/km ( $\lambda = 570 \text{ nm}$ ) or 125 - 150 dB/km ( $\lambda = 650 \text{ nm}$ ).

10 The fluorine-containing polymers used as the cladding material or as the material for the outer cladding layer may be pure polymers, copolymers of fluorine-containing monomers as well as copolymers of fluorine-containing monomers with acrylic acid and acrylates as well as mixtures of such polymers or copolymers. Vinylidene fluoride, tetrafluoroethylene, hexafluoropropene, methacrylic acid-tetrafluoropropylester, methacrylic acid-pentafluoropropylester, methacrylic acid-trifluoroethylester, methacrylic acid-heptadecafluorododecylester as well as mixtures or copolymerisates thereof, alternatively also acrylic acid- or acrylate-modified polymers, copolymers or polymer mixtures may be used in particular.

15 20 The outer diameters of the fiber core 2 and the fiber cladding 3 meet the standard specified in IEC 60 793-2 (outer diameter of cladding  $\mathcal{O}_{\text{cladding}} = 1000 \pm 60 \mu\text{m}$ , the core diameter  $\mathcal{O}_{\text{core}}$  should typically be smaller than  $\mathcal{O}_{\text{cladding}}$  by 10 - 20  $\mu\text{m}$ ; numerical aperture  $0.5 \pm 0.15$ ). It is of course also possible to select the dimensions of the fiber core 2 and the fiber cladding 3 according to the other standard values ( $\mathcal{O}_{\text{cladding}} = 750 \pm 45 \mu\text{m}$  or  $500 \pm 30 \mu\text{m}$ ) or to adapt the dimensions to the commercial step index profile plastic optical fibers ( $\mathcal{O}_{\text{cladding}} = 75 \mu\text{m} / 125 \mu\text{m} / 250 \mu\text{m} / 380 \mu\text{m} / 1500 \mu\text{m} / 2000 \mu\text{m} / 3000 \mu\text{m}$ ).

25 30 The moulding material enclosing the plastic optical fiber which is applied by co- or tandem extrusion protects the sensitive plastic optical fiber 2, 3 from outer influences. Its thickness is selected according to the above standard such that the outer diameter of the wave-guide  $\mathcal{O}_{\text{wave-guide}}$  is  $2.2 \pm 0.1 \text{ mm}$  ( $\mathcal{O}_{\text{cladding}} = 1000 \mu\text{m}$  or  $\mathcal{O}_{\text{cladding}} = 750 \mu\text{m}$ ) or  $\mathcal{O}_{\text{wave-guide}} = 1.5 \pm 0.1 \text{ mm}$  ( $\mathcal{O}_{\text{cladding}} = 500 \mu\text{m}$ ).

The moulding material 4 which is used as the protective sheathing and particularly well adheres to the fluorine-containing polymer of the fiber cladding 3 is made of a modified PA whose maximum concentration of carboxylic terminal groups is 15  $\mu\text{eq/g}$  and whose concentration of amino terminal groups is in the range of 50 - 300  $\mu\text{eq/g}$ . The above concentration of amino terminal groups is adjusted by an aminic chain transfer agent added to the not yet completely polymerized PA (single polymerization of the chain transfer agent). Examples of chain transfer agents are hexyl amine, octyl amine, ethyl hexyl amine, tridecyl amine, dibutyl amine, stearyl amine and other aliphatic, cycloaliphatic or aromatic monoamines having 2 - 44 C atoms, in particular 4 - 36 C atoms, as well as diamines such as 1,4-diaminobutane, 1,6-diaminohexane, diaminocyclohexane, 1,10-diaminodecane, 1,12-diaminododecane, m- or p-xylylene diamine, cyclohexyl dimethylene diamine, bis-(p-aminocyclohexyl) methane as well as other aliphatic, cycloaliphatic or aromatic amines having 2 - 44 C atoms, in particular 6 - 36 C atoms, and the excess of an aminic difunctional monomer which is the main component of the polyamide.

Suitable polyamides for the purposes of the invention are homo- and copolyamides which can be processed at sufficiently low temperatures, i. e. at a maximum of 220 °C, so as not to damage the cladding and fiber core of the plastic optical fiber. According to the invention it is essential that the polyamides used have a relative viscosity below 2.0, in particular below 1.8 and particularly preferably 1.4 - 1.8 (relative viscosity: 0.5 % measured in m-cresol at 20 °C).

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Such polyamides may also be made up of polyamide-forming monomers such as caprolactam, laurine lactam, amino hexanoic acid, amino undecanoic acid, dodecanedioic acid, dimeric acid, terephthalic acid, isophthalic acid, cyclohexane dicarboxylic acid, naphthalene dicarboxylic acid, tert-butyl isophthalic acid, phenylindane dicarboxylic acid, diaminobutane, hexamethylene diamine, methyl pentamethylene diamine, 3,3-dimethyl-4,4-xylylene diamine, 2,2-bis(p-aminocyclohexyl) propane, bis(p-aminocyclohexyl) methane, isophorone diamine, polypropyleneglycol diamine, norbonane diamine, 1,3-bis(aminomethyl) cyclohexane, TCD diamine if they have a melting point up to a maximum of 220 °C, preferably below 210 °C and particularly preferably below 200 °C. These include according to the invention in particular PA 11, PA 12, PA 610, PA 612, PA 1212 or the copolyamides PA 6/12, PA 6/9/6, PA 6/9/12, PA 610/6, PA 610/11, PA 610/12, PA 612/6, PA 612/11, PA 612/12 or mixtures thereof, PA 12 being particularly preferred.

To the polyamides having the above structure, normal additives such as UV and heat stabilizers, crystallization promoters, softeners, flameproofing agents, external lubricants, and anorganic fillers may be added.

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The following method was used to test the adherence of the protective sheathing 4 made of a modified polyamide to the fiber cladding 3:

- partial shouldering of the protective sheathing of a wave-guide approx. 500 mm in length in such a way that the length of the remaining protective sheathing is approx. 30 mm;
- leading the shouldered portion of the wave-guide through the hole of a plate, the diameter of the hole being  $\approx$ 1.1 mm which is somewhat larger than the outer diameter of the fiber cladding;
- chucking the shouldered end of the wave-guide into a tensile testing machine (drawing-off rate: 10 mm/min); and
- measuring the tensile force at which the protective sheathing becomes detached from the cladding of the plastic optical fiber.

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The PA 12 types given in the Table below were subjected to the test.

Polymer	Concentration of NH <sub>2</sub> terminal groups	Concentration of COOH terminal groups	Relative viscosity: 0.5 % in m-cresol at 20 °C	
PA No. 1	10	95	1.65	PA not according to the invention
PA No. 2	95	<15	1.66	PA according to the invention
PA No. 3	134	<5	1.58	PA according to the invention
PA No. 4	173	<5	1.47	PA according to the invention

The test showed that the tensile force required for stripping the protective sheathing made of PA No. 1 amounted to a minimum of 11 N (no adherence), typically 40 - 50 N and a maximum of 51 N, due to the very different adherence of the protective sheathing to the respective plastic optical fiber from specimen to specimen. The stripping forces measured for wave-guides with the protective PA sheathings according to the invention ranged from 68 - 75 N and hence varied to a clearly less extent. The measured maximum value of the stripping force of 75 N is surprising all the more as the extrusion temperature for the moulding material making up the protective sheathing was to amount to only approx. 185 - 200 °C due to the comparatively low glass-transition temperature of the PMMA ( $T_G \approx 100 - 110$  °C) used as the core material.

A comparatively large stripping force was also measured for an optical wave-guide whose protective sheathing was made of the PA disclosed in EP 0 767 190 A1. However, this PA is not suitable for the above applications, as the heat storage (24 hours at 80 °C) of wave-guides having an equivalent structure resulted in a browning of the outer cladding area.

The following three typical examples of wave-guides ( $\mathcal{O}_{\text{cladding}} = 1000$  µm,  $\mathcal{O}_{\text{protective sheathing}} = 2.2$  mm) were tested:

1) Optical wave-guide: type SB-1000, Asahi Chemical Industry Co., Ltd.;  
 moulding material: Grilamid L16A (PA according to the invention),  
 EMS-Chemie AG, CH -7013 Domat/Ems.

Processing temperature of the moulding material:  $T = 190$  °C,  
 processing speed: 60 m/min,  
 stripping force: 68 - 75 N (average: 73 N).

2) Optical wave-guide: SB-1000;  
 moulding material: Grilamid L16LM (PA not according to the invention),  
 EMS-Chemie AG.

Processing temperature:  $T = 190$  °C,  
 processing speed: 60 m/min,  
 stripping force: 48 - 51 N (average: 49 N).

3) Optical wave-guide: type TB-1000, Asahi Chemical Industry Co., Ltd.;  
moulding material: Grilamid L16LM (PA not according to the invention).  
Processing temperature:  $T = 190 \text{ }^{\circ}\text{C}$ ,  
5 processing speed: 60 m/min,  
stripping force: 7 - 18 N (average: 11 N).

It is to be understood that the invention is not limited to the embodiments described above.  
Without deviating from the scope of the invention, it is therefore possible

- to give the protective sheathing 4 of the optical wave-guide 1 a multilayer structure (see particularly WO 99/1203) or to provide it with a PVC cladding of  $\approx 1 - 2 \text{ mm}$  in thickness;
- to embed reinforcing elements, in particular glass fibers, carbon fibers or mineral fibers, in the protective sheathing 4;
- to admix fillers (carbon black, talcum, etc.) to the protective sheathing material; and
- to use one or several of the optical wave-guides 1 as light transmitting elements in the simplex, duplex, twin or hybrid cables known from A. Weinert: Kunststofflichtwellenleiter - Grundlagen, Komponenten, Installation (Plastic optical fibers: Fundamentals, Components, Installation), Publicis MCD Verlag, 1998, pp. 55  
20 - 62.

Patent claims

1. Optical wave-guide (1) comprising a plastic optical fiber (2, 3) including a fiber core (2) and a fiber cladding (3) having a single- or multilayer structure, and at least one protective sheathing (4) enclosing the plastic optical fiber (2, 3), the fiber cladding (3) or at least its outer layer being made of a fluorine-containing plastic and the protective sheathing (4) being made of polyamide in which  
5 the protective sheathing (4) is made of polyamides or copolyamides or mixtures thereof having a melting point of less than 220 °C and is self-adhesively applied to the fiber cladding (3),  
the maximum concentration of the carboxyl terminal groups of the polyamide being 15  
10  $\mu\text{eq/g}$  and the concentration of the amino terminal groups being in the range of 50  $\mu\text{eq/g}$  to 300  $\mu\text{eq/g}$ .
2. Optical wave-guide as claimed in Claim 1 in which the polyamides or copolyamides or mixtures thereof have a melting point of less than 210 °C and particularly preferably less than 200 °C.
3. Optical wave-guide as claimed in Claim 1 or 2 in which the polyamides are selected from  
20 the group consisting of PA 11, PA 12, PA 610, PA 612, PA 1212 or the copolyamides PA 6/12, PA 6/9/6, PA 6/9/12, PA 610/6, PA 610/11, PA 610/12, PA 612/6, PA 612/11, PA 612/12 or mixtures thereof, PA 12 being particularly preferred.
4. Optical wave-guide as claimed in any one of Claims 1 to 3 in which the maximum  
25 concentration of the carboxyl terminal groups of the polyamide is 15  $\mu\text{eq/g}$  and the concentration of the amino terminal groups is in the range of 90  $\mu\text{eq/g}$  to 250  $\mu\text{eq/g}$ .
5. Optical wave-guide as claimed in Claims 1 to 4 in which the concentration of the amino  
30 terminal groups is adjusted by the addition of mono- or difunctional amines or by the excess of a diamine component making up the polyamide.

6. Optical wave-guide as claimed in Claims 1 to 5 in which the polyamide includes at least one additive from the group consisting of UV stabilizer, heat stabilizer, crystallization promoter, softener, flameproofing agent, external lubricant and organic filler.

5 7. Optical wave-guide as claimed in Claims 1 to 6 in which the fiber cladding (3) is made of vinylidene fluoride, tetrafluoroethylene, hexafluoropropene, methacrylic acid-tetrafluoropropylester, methacrylic acid-pentafluoropropylester, methacrylic acid-trifluoroethylester, methacrylic acid-heptadecafluorododecylester as well as mixtures or copolymerisates of the above substances, alternatively also of acrylic acid- or acrylate-modified polymers, copolymers or polymer mixtures.

10 8. Optical wave-guide as claimed in Claims 1 to 7 in which the fiber core (2) is made of polymethyl methacrylate (PMMA).

15 9. Optical wave-guide as claimed in Claims 1 to 8 in which the outer diameter of the plastic optical fiber (2, 3) is in the range of 75 - 3000  $\mu\text{m}$ .

10. Optical wave-guide as claimed in Claims 1 to 9 in which the outer diameter of the fiber cladding (3) is  $1000 \pm 60 \mu\text{m}$  or  $750 \pm 45 \mu\text{m}$  or  $500 \pm 30 \mu\text{m}$ .

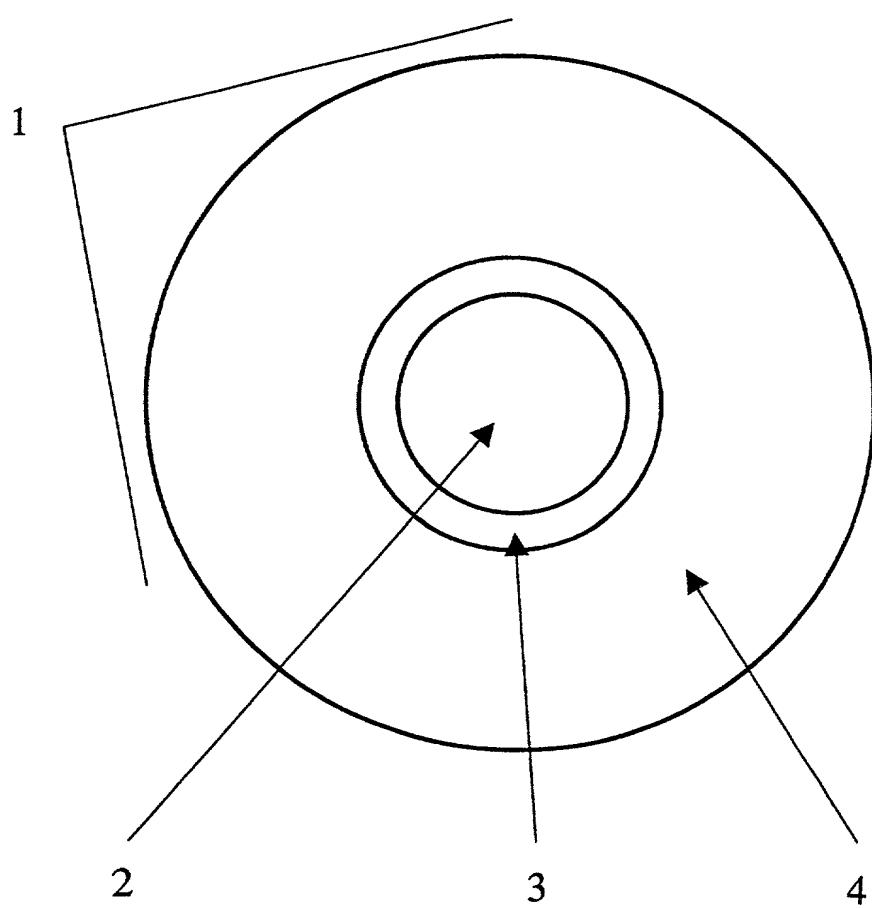
20 11. Optical wave-guide as claimed in Claims 1 to 10 in which the diameter of the fiber core (2) is smaller than the corresponding outer diameter of the fiber cladding (3) by approx. 10 to 20  $\mu\text{m}$ .

25 12. Optical wave-guide as claimed in any one of the preceding Claims 1 to 11 in which the outer diameter of the optical wave-guide (1) is in the range of 0.15 mm to 5.0 mm.

09/937817

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**Fig. 1**



COMBINED DECLARATION AND POWER OF ATTORNEY  
FOR PATENT APPLICATION

Attorney Docket  
Number: 25045-11

DECLARATION: As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**OPTICAL WAVE-GUIDE**

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is attached hereto.

was filed on 30 March 2000 as PCT Application Number PCT/EP00/02831 and amended on \_\_\_\_\_  
(if applicable.)

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Priority Claimed

<u>19914743.4</u> (Number)	<u>DE</u> (Country)	<u>(31/03/99)</u> Filed (Day/Month/Year)	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
<u></u> (Number)	<u></u> (Country)	<u></u> Filed (Day/Month/Year)	<input type="checkbox"/> Yes <input checked="" type="checkbox"/> No

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below:

<u>(Application Serial No.)</u>	<u>(Filing Date)</u>	<u>(Application Serial No.)</u>	<u>(Filing Date)</u>
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SEND ALL CORRESPONDENCE TO: Michael A. Mann, NEXSEN PRUET JACOBS & POLLARD, LLC, P.O. Drawer 2426, Columbia, South Carolina, 29202 TELEPHONE NUMBER: (803) 771-8900

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FULL NAME OF FIRST INVENTOR (given name, family name) Hans-Matthias HORN  
Complete Post Office Address Regerweg 5, D-96465 Neustadt GERMANY  
City and Country of Residence Neustadt GERMANY Citizenship DE

Inventor's Signature Hans-Matthias Horn Date 9.11.2001

**COMBINED DECLARATION AND POWER OF ATTORNEY  
FOR PATENT APPLICATION**

Attorney Docket  
Number:

**PAGE 2**

2 - 00

FULL NAME OF SECOND JOINT INVENTOR Joachim SCHAEFER  
Complete Post Office Address Obere Birkleite 15, D-96465 Neustadt GERMANY DE  
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Inventor's Signature J. Schaefer Date 9.11.2001

3 - 00

FULL NAME OF THIRD JOINT INVENTOR Ilona SCHMIDT  
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City and Country of Residence Neustadt GERMANY Citizenship DE

Inventor's Signature Ilona Schmidt Date 11-17-01

4 - 00

FULL NAME OF FOURTH JOINT INVENTOR Helmut THULLEN  
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Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

5 - 00

FULL NAME OF FIFTH JOINT INVENTOR Volker EICHHORN  
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City and Country of Residence Chur SWITZERLAND Citizenship DE

Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

6 - 00

FULL NAME OF SIXTH JOINT INVENTOR Thomas WUTKE  
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City and Country of Residence Waldbröl GERMANY Citizenship DE

Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

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Complete Post Office Address Am Tau 2, D-96465 Neustadt GERMANY  
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Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

4-cc  
FULL NAME OF FOURTH JOINT INVENTOR Helmut THULLEN  
Complete Post Office Address Versamerstrasse 39, CH-7402 Bonaduz SWITZERLAND CHX  
City and Country of Residence Bonaduz SWITZERLAND Citizenship DE

Inventor's Signature Helmut Thullen Date September 24th, 2001

FULL NAME OF FIFTH JOINT INVENTOR Volker EICHHORN  
Complete Post Office Address Ringstrasse 170, CH-7000 Chur SWITZERLAND  
City and Country of Residence Chur SWITZERLAND Citizenship DE

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Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

*S-00*

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City and Country of Residence Waldbröl GERMANY Citizenship DE

Inventor's Signature *Th. Wutke* Date 01.10.2001

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7-100

FULL NAME OF SEVENTH JOINT INVENTOR Georg STOEPPELMANN  
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City and Country of Residence Bonaduz SWITZERLAND Citizenship DE

Inventor's Signature



Date 24.9.2001

FULL NAME OF EIGHTH JOINT INVENTOR

Complete Post Office Address \_\_\_\_\_  
City and Country of Residence \_\_\_\_\_ Citizenship \_\_\_\_\_

Inventor's Signature

Date \_\_\_\_\_

FULL NAME OF NINETH JOINT INVENTOR

Complete Post Office Address \_\_\_\_\_  
City and Country of Residence \_\_\_\_\_ Citizenship \_\_\_\_\_

Inventor's Signature

Date \_\_\_\_\_

FULL NAME OF TENTH JOINT INVENTOR

Complete Post Office Address \_\_\_\_\_  
City and Country of Residence \_\_\_\_\_ Citizenship \_\_\_\_\_

Inventor's Signature

Date \_\_\_\_\_

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FULL NAME OF SEVENTH JOINT INVENTOR Georg STOEPPELMANN  
Complete Post Office Address Via Sableun 2, CH-7402 Bonaduz SWITZERLAND  
City and Country of Residence Bonaduz SWITZERLAND Citizenship DE

Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

FULL NAME OF EIGTH JOINT INVENTOR \_\_\_\_\_  
Complete Post Office Address \_\_\_\_\_  
City and Country of Residence \_\_\_\_\_ Citizenship \_\_\_\_\_

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3

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**PAGE 3**

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Complete Post Office Address Via Sableun 2, CH-7402 Bonaduz SWITZERLAND  
City and Country of Residence Bonaduz SWITZERLAND Citizenship DE

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City and Country of Residence Bonaduz SWITZERLAND Citizenship DE

Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

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Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

FULL NAME OF NINETH JOINT INVENTOR \_\_\_\_\_  
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Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

FULL NAME OF TENTH JOINT INVENTOR \_\_\_\_\_  
Complete Post Office Address \_\_\_\_\_  
City and Country of Residence \_\_\_\_\_ Citizenship \_\_\_\_\_

Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

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Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

FULL NAME OF THIRD JOINT INVENTOR Ilona SCHMIDT  
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Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

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Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

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Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

S

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**POWER OF ATTORNEY:** I hereby appoint the following attorneys and/or agents to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: Joseph T. Guy, Reg. No. 35,172; John B. Hardaway, III, Reg. No. 26,554; William Y. Klett, III, Reg. No. 41,903; Michael A. Mann, Reg. No. 32,825; J. Herbert O'Toole, Reg. No. 31,404; Timothy J. Slabouz, Reg. No. 47,949; Charles L. Schwab, Reg. No. 17,497; Oscar A. Towler, III, Reg. No. 33,803;

SEND ALL CORRESPONDENCE TO: Michael A. Mann, NEXSEN PRUET JACOBS & POLLARD, LLC, P.O. Drawer 2426, Columbia, South Carolina, 29202 TELEPHONE NUMBER: (803) 771-8900

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

FULL NAME OF FIRST INVENTOR (given name, family name) Hans-Matthias HORN

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City and Country of Residence Neustadt GERMANY

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Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

**COMBINED DECLARATION AND POWER OF ATTORNEY  
FOR PATENT APPLICATION**

Attorney Docket  
Number:

**PAGE 3**

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Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

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Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

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Complete Post Office Address \_\_\_\_\_  
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Inventor's Signature \_\_\_\_\_ Date \_\_\_\_\_

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**COMBINED DECLARATION AND POWER OF ATTORNEY  
FOR PATENT APPLICATION**

Attorney Docket  
Number: 25045-11

**DECLARATION:** As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**OPTICAL WAVE-GUIDE**

the specification of which:

is attached hereto.

was filed on 30 March 2000 as PCT Application Number PCT/EP00/02831 and amended on \_\_\_\_\_  
(if applicable.)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119 (a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States listed below, and have also identified below any foreign application for patent or inventor's certificate or PCT international application having a filing date before that of the application on which priority is claimed:

Priority Claimed

<u>199.14 743.4</u> (Number)	<u>DE</u> (Country)	<u>(31/03/99)</u> Filed (Day/Month/Year)	<input checked="" type="checkbox"/> Yes	<input type="checkbox"/> No
<u></u> (Number)	<u></u> (Country)	<u></u> Filed (Day/Month/Year)	<input type="checkbox"/> Yes	<input type="checkbox"/> No

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below:

<u>(Application Serial No.)</u>	<u>(Filing Date)</u>	<u>(Application Serial No.)</u>	<u>(Filing Date)</u>
I hereby claim the benefit under 35 U.S.C. §120 of any United States application(s) or §365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT application(s) in the manner provided by the first paragraph of 35 U.S.C. §112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56 which became available between the filing date of the prior application(s) and the national or PCT international filing date of this application:			
<u>(Application Serial No.)</u>	<u>(Filing Date)</u>	<u>(Status - patented, pending, abandoned)</u>	

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